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Vapor-Phase Ammoxidation of 5-Membered Heterocyclic Compounds. Ammoxidation of Furfural and 2-Thiophenealdehyde

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The kinetics and mechanism of vapor-phase ammoxidation of furfural to 2-furonitrile, and of 2-thiophenealdehyde to 2-thiophenenitrile, were studied over the Mo–Bi–Sb catalyst (molar ratio 3 : 5 : 2) in an integral flow fixed bed reactor under atmospheric pressure. The reaction temperature was 390° for furfural and 400° for 2-thiophenealdehyde. In both cases, the selectivity of nitrile was maximum with high conversion of aldehyde and the by-products formed were negligible in amounts.

The reaction rate depended on the partial pressure of aldehyde and oxygen, but unaffected by that of ammonia. Model fitting was tried by the non-linear least square method, and the experimental data were well interpreted by the Langmuir-Hinshelwood mechanism, where the rate controlling step was the surface reaction between adsorbed aldehyde molecules and adsorbed oxygen molecules.

Keywords——ammoxidation; kinetics; mechanism; furfural; 2-thiophenealdehyde; catalyst

Ammoxidation is a catalytic process in which the reactant (aldehyde or alkyl group) undergoes oxidation and ammonolysis and combines to form nitrile.

The nitriles of 5-membered heterocyclic compounds are very useful. For example, 2-furonitrile has been reported to be 100 times sweeter than suger and hence is used as a synthetic sweeting agent for low calorie foods and drinks. It is also useful in extractive distillation. Therefore, it is very interesting to synthesize them easily by ammoxidation. Although, several workers[2,3] have studied the vapor-phase ammoxidation of 5-membered heterocyclic compounds, there is little information about the catalyst, process conditions and mechanism.

Usually, alkyl compounds are used as raw material for vapor-phase ammoxidation, but in the case of 5-membered heterocyclic compounds, aldehydes are more cheaply available than alkyl compounds.

The purpose of the present work was to investigate a suitable catalyst for the ammoxidation of furfural and 2-thiophenealdehyde and to obtain accurate kinetic data over a wide range of reactant concentrations, as well as to provide some insight into the reaction mechanism.

Experimental

Materials——Furfural was obtained from Wako Pure Chemical Industries Ltd, and 2-thiophenealdehyde was obtained from Tokyo Kasei Kogyo Co., Ltd. These were further purified by vacuum distillation and their purity was determined by gas chromatography. Nitrogen, oxygen and ammonia were dried by the passage through beds packed with NaOH and sodalime.

Catalyst——The catalyst employed in this study was Mo–Bi–Sb, in the molar ratio of 3 : 5 : 2, was prepared by mixing an aqueous solution of antimony trichloride with the solution of ammonium molybdate in 28% ammonia solution. The resulting solution was heated with agitation to evolve ammonium chloride, cooled

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[2] T.J. Jennings (to Shell Oil Company), U.S. Patent 3260731 (July 12, 1966).

[3] A.V. Minibaev, L.N. Khabibullina, A.R. Kuzyev, A.Kh. Yangurazov, G.A. Tolstikov, and S.R. Rafikov, *Zhurnal Organicheskoi Khimii*, 7, 377 (1971).

and to this solution was added with stirring, a solution of bismuth nitrate prepared in 60% HNO_3. On heating, nitric oxide evolved and the salts decomposed leaving behind their metallic oxides, which were later calcined in air at 550° for 6 hours. The material was pelleted and then crushed to the desired particle size.

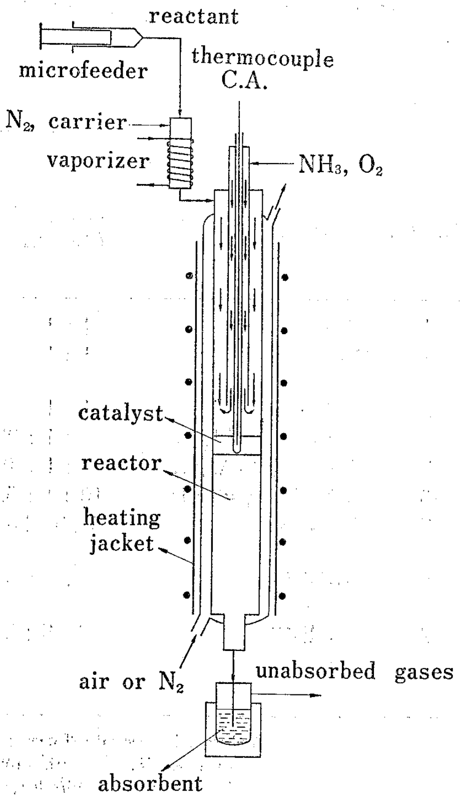

Fig. 1. Flow Diagram

Experimental Apparatus——The apparatus as shown in Fig. 1 consists of four main units: feeding system for introducing controlled amounts of nitrogen, oxygen, ammonia and aldehyde; preheater; main reactor and product recovery unit.

(a) Feeding System: Purified N_2 metered by means of a flow meter, was used to carry away the vapor of aldehyde from the preheater to the main reactor. Purified oxygen and ammonia as metered by means of flow meters, were mixed and finally fed to the main reactor.

(b) Preheater: A preheater, 1.7 cm in internal diameter and 24 cm long, packed with glass wool, was used to preheat the incoming aldehyde upto 200°. The vapor of aldehyde so formed, were carried away by the inert carrier gas, N_2, from the preheater to the main glass reactor.

(c) Reactor: The reactor, 1.6 cm in internal diameter and 67 cm long, consisted of a preheating zone and the catalyst zone. The catalyst was packed over a plug of purified glass wool which was supported by means of glass bead packing. The thermocouple was inserted through a concentric glass tube for measuring the temperature of catalyst bed. The reactor was sealed by jacketted tube of 1.8 cm in internal diameter, through which the controlled amounts of air could be passed to maintain the uniform constant temperature across the catalyst bed and as well as to have easy temperature control of the reactor. The main feature of this reactor was that the gases, ammonia and oxygen, were allowed to flow through the concentric tube from a separate line and kept away from the vapor of aldehyde inside the main reactor, until finally they came to contact near the surface of the catalyst bed. The flow rates of the gases (N_2, NH_3 and O_2) were adjusted in such a way so that the time of contact between aldehyde and ammonia vapors should not exceed more than 0.002 second to avoid the formation of undesirable products.

(d) Product Recovery: The reaction products were absorbed in a vessel containing dioxane solvent, whereas the unabsorbed gases were collected over an aspirator bottle.

Procedure——Experiments were conducted in an integral reactor operated with high conversion of aldehyde at atmospheric pressure. Initially, standard runs were carried out periodically to check the activity of the used catalyst. The reproducibility was found to be within 5% at high aldehyde conversion. Temperature gradients across the catalyst bed were small enough to be neglected. The activity of the catalyst was found to remain fairly constant during the course of the present study.

Mass transfer, both external and within the catalyst particles, was estimated to be sufficiently rapid that the reaction rate is not affected. The effect of partial pressure of ammonia, oxygen, aldehyde and water on the reaction rate was studied at 390° in the case of furfural and 400° in the case of 2-thiophenealdehyde. The effect of temperature was also investigated.

Identification and Analysis——At high aldehyde conversion, the selectivity of nitrile (2-furonitrile or 2-thiophenenitrile) was above 95%. The traces of 2-furfuraldehyde oxime or 2-thiophenealdehyde oxime and carbon dioxide were also formed. These products were identified by gas-liquid chromatography (GLC) and infrared (IR) spectra.

The analysis of reaction mixture was done by GLC (Shimadzu GC-3BT). The analysis of furfural and 2-furonitrile was conducted by using a 2.1 m long glass column (3 mm i.d.) packed with 10% polyethylene glycol adipate on Neopack 1A (60/80 mesh), whereas the analysis of 2-thiophenealdehyde and 2-thiophenenitrile was made by using a similar glass column packed with 20% 1,2,3-tris(2-cyanoethoxy)propane on Neosorb NC (60/80 mesh). The gaseous products were analyzed by using a 2 m long stainless steel column (3 mm i.d.) packed with activated charcoal (60/80 mesh).

Results and Discussion

Comparison of Catalysts

The typical catalyst of vapor-phase ammoxidation is bismuth molybdate for propylene and vanadium pentoxide for aromatic or heteroaromatic compounds. In this study, both catalyst systems were compared, and their results have been shown in Table I. The vanadium pentoxide catalysts are so active that the decarbonylation occurs, and the production of carbon dioxide is high. Therefore, for this reaction, the bismuth molybdate catalyst is more suitable.

Table I. Effect of Different Catalysts

S. No.	Catalyst	Composition (mol ratio)	Weight of catalyst (g)	Reaction temp. (°C)	Furfural (g-mol/hr) ×10³	Yield (%)	Select. (%)	CO_2 evolved (g-mol/hr) ×10⁴
1	Bi-Sb	1 : 1	1.5	390	9.500	18.52	31.56	22.37
2	Bi-Mo	1 : 1	1.5	390	9.723	44.83	83.85	4.940
				430	9.700	78.45	88.95	6.215
3	Sb-Mo	1 : 1	1.5	390	9.706	23.97	52.08	7.257
4	V_2O_5-MoO_3-Al_2O_3	4 : 1 : 95[a]	1.5	390	9.500	50.34	52.15	52.05
5	Sb_2O_3-V_2O_5-Al_2O_3	4 : 1 : 45[a]	1.5	390	9.500	37.10	47.21	18.25
6	V_2O_5-Cr_2O_3-pumice	10 : 1 : 89[a]	1.5	390	9.500	58.02	73.76	6.726
7	V-Bi-Sb	32.5 : 50 : 17.5	1.5	390	9.500	60.50	65.78	28.85
				430	9.500	52.18	55.80	46.12
8	Mo-Bi-Sb	2 : 5 : 3	1.5	390	9.500	31.62	73.68	1.259
				430	9.531	45.51	85.43	1.487
9	Mo-Bi-Sb	2 : 5 : 3	6.0	390	9.594	91.99	99.25	Nil
				375	8.884[b]	92.83	97.88	Nil
				450	8.943[b]	95.30	99.79	Nil

Volumetric flow rate of gases:
No. 1—8: N_2; 276.3 (ml/min), O_2; 35.5 (ml/min), NH_3; 6.0 (ml/min).
No. 9: N_2; 236.3 (ml/min), O_2; 75.5 (ml/min), NH_3; 6.0 (ml/min).
a) Weight ratio. *b*) 2-Thiophene aldehyde.

K. Ohdan *et al.*[4] reported that the addition of antimony oxide to bismuth molybdate was valid to the activity and the selectivity. The addition of antimony oxide was also studied with changing molar ratio of Mo, Bi and Sb. In this reaction, the addition is effective and the most suitable catalyst is the mixed oxide catalyst, Mo-Bi-Sb (molar ratio 2: 5: 3). The yield of 2-furonitrile or 2-thiophenenitrile is very high and the production of carbon dioxide is negligible.

From these results, this catalyst was selected for the present work.

Effects of Mass Transfer

The yield of furonitrile or thiophenenitrile is not affected with the flow rate and the catalyst particle size. Hence, the mass transfer, both external and intraparticle diffusion, is sufficiently rapid that the rate determining step of these reactions in the range studied, may be the chemical reaction step.

Effects of Partial Pressure

The effect of partial pressure of ammonia on the yield of nitrile formation is shown in Fig. 2. As the yield of nitriles at different partial pressure remains unaffected, therefore, the reaction rate is independent to the partial pressure of ammonia.

Figure 3 shows the effect of oxygen partial pressure on the yield. The prominent feature of Fig. 3 is that the yield of nitriles increases with increasing oxygen partial pressure, then tended to become constant, and finally decreased slightly at higher oxygen pressure.

Figure 4 representing the effect of partial pressure of aldehyde at constant partial pressure of oxygen and ammonia, indicates that the yield of nitrile goes on decreasing gradually with

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[4] K. Ohdan, S. Umemura, and K. Yamada, *Kogyo-kagaku-zasshi*, 72, 2376 (1969).

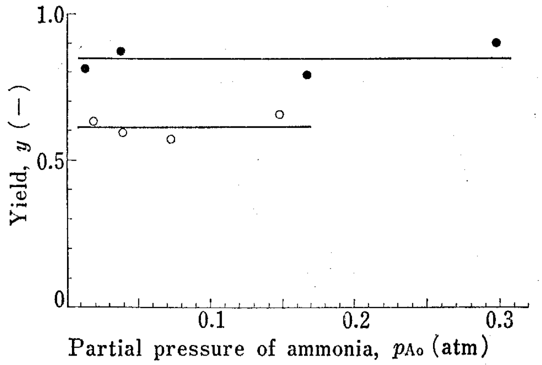


Fig. 2. Effect of Partial Pressure of Ammonia

—●—: yield of 2-furonitrile.
Reaction temp. 390°, $p_{R_0}=0.0123$ (atm), $p_{B_0}=0.235$ (atm), $W/F=14.82$ (g-cat·hr/gmol), $W=6$(g)
—○—: yield of 2-thiophenenitrile.
Reaction temp. 400°, $p_{R_0}=0.0115$ (atm), $p_{B_0}=0.235$ (atm), $W/F=2.52$ (g-cat·hr/gmol), $W=2$(g).

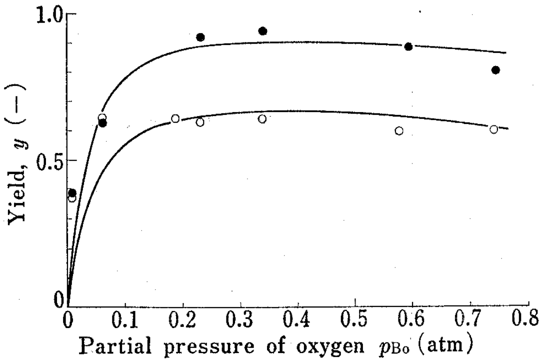


Fig. 3. Effect of Partial Pressure of Oxygen

—●—: yield of 2-furonitrile.
Rection temp. 390°, $p_{R_0}=0.0123$ (atm), $p_{A_0}=0.0190$ (atm), $W/F=7.70$ (g-cat·hr/gmol), $W=6$(g).
—○—: yield of 2-thiophenenitrile.
Reaction temp. 400°, $p_{R_0}=0.0115$ (atm), $p_{A_0}=0.0190$ (atm), $W/F=2.52$ (g-cat·hr/gmol), $W=2$(g).

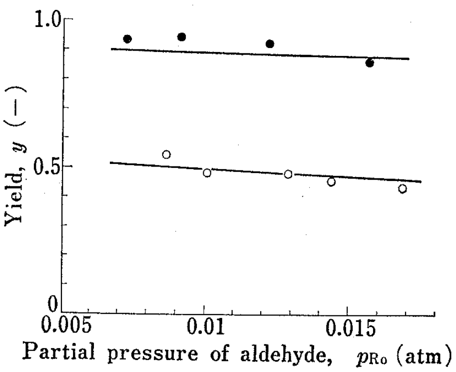


Fig. 4. Effect of Partial Pressure of Aldehyde

—●—: yield of 2-furonitrile.
Reaction temp. 390°, $p_{B_0}=0.235$ (atm), $p_{A_0}=0.0190$ (atm), $W/F=7.70$ (g-cat·hr/gmol), $W=6$(g).
—○—: yield of 2-thiophenenitrile.
Reaction temp. 400°, $p_{B_0}=0.235$ (atm), $p_{A_0}=0.0190$ (atm), $W/F=1.89$ (g-cat·hr/g-mol), $W=1.5$ (g).

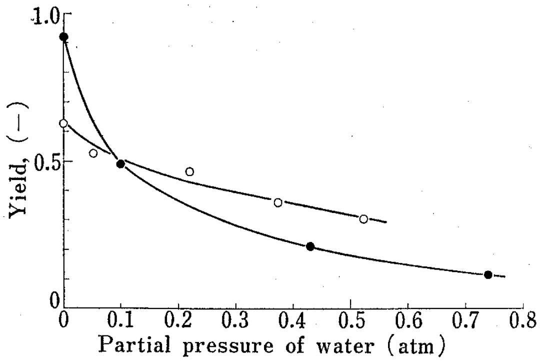


Fig. 5. Effect of Partial Pressure of Water

—●—: yield of 2-furonitrile.
Reaction temp. 410°, $p_{R_0}=0.0123$ (atm), $p_{A_0}=0.0190$ (atm), $p_{B_0}=0.235$ (atm), $W/F=14.81$ (g-cat·hr/gmol), $W=6$(g).
—○—: yield of 2-thiophenenitrile.
Reaction temp. 400°, $p_{R_0}=0.0115$ (atm), $p_{A_0}=0.0190$ (atm), $p_{B_0}=0.235$ (atm), $W/F=2.52$ (g-cat·hr/gmol), $W=2$(g).

the increase in partial pressure of aldehyde. However, this decrease in the yield of nitrile is not too large.

The effect of the successive additions of water on the yield of nitrile formation have been shown in Fig. 5, which shows that the yield of nitrile goes on decreasing with the increase in the partial pressure of water. Consequently, the rate of reaction decreases with the increase in partial pressure of water.

Effect of Reaction Temperature

The effect of temperature on the aldehyde conversion and yield of nitrile was investigated between 250° and 450° and is shown in Fig. 6. The conversion and the yield increases with the rise in temperature. The yield as well as the selectivity of nitriles become maximum at higher reactants conversion. At higher temperature, the yield of 2-thiophenenitrile is almost constant, while the yield of furonitrile decreases. This difference depends on the stability of nitrile and hence, 2-thiophenenitrile is more stable than furonitrile at higher temperature.

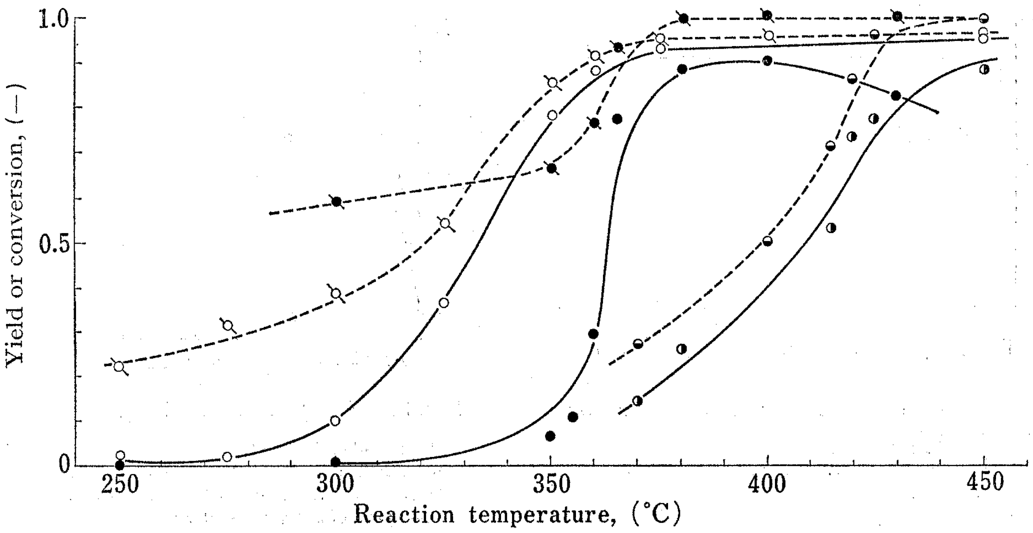


Fig. 6. Effect of Reaction Temperature

---●---: conversion of furfural; —●—: yield of 2-furonitrile.
$p_{R_0}=0.0138$ (atm), $p_{B_0}=0.181$ (atm), $p_{A_0}=0.0376$ (atm), $W/F=14.82$ (g-cat•hr/gmol), $W=6$(g).
---◒---: conversion of furfural; —◑—: yield of 2-furonitrile.
$p_{R_0}=0.0459$ (atm), $p_{B_0}=0.172$ (atm), $p_{A_0}=0.0366$ (atm), $W/F=14.75$ (g-cat·hr/gmol), $W=6$(g).
---○---: conversion of 2-thiophenealdehyde; —○—: yield of 2-thiophenenitrile.
$p_{R_0}=0.0115$ (atm), $p_{B_0}=0.235$ (atm), $p_{A_0}=0.0190$ (atm), $W/F=7.57$ (g-cat·hr/gmol), $W=6$(g).

Kinetic Evaluation

From the above mentioned results, the mass transfer, external and internal diffusion is negligible, and desorption of products is not the rate determining step of this reaction. Therefore, the rate determining step of this reaction can be assumed to be the surface reaction.

The several reaction models were compared by means of the non-linear least square method[5,6] and finally the experimental data were found to be well interpreted by the Langmuir-Hinshelwood mechanism, in which the surface oxidation of aldehyde was assumed to the rate controlling step and later the reaction with ammonia proceded to form nitrile. The model assumed for furfural or 2-thiophenealdehyde ammoxidation is represented by Equations (1) to (8):

$$\text{RCHO} + \text{s} \overset{K_R}{\rightleftarrows} \text{RCHO*} \tag{1}$$

$$\text{O}_2 + \text{s} \overset{K_B}{\rightleftarrows} \text{O}_2\text{*} \tag{2}$$

$$\text{RCHO*} + \text{O}_2\text{*} \xrightarrow{k} (\text{RCHO-O}_2)\text{* unknown intermediate} \tag{3}$$

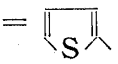
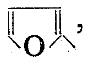
$$(\text{RCHO-O}_2)\text{*} + \text{NH}_3 \rightleftarrows \text{RCH=NOH*} + \text{H}_2\text{O}_2\text{*} \tag{4}$$

$$\text{RCH=NOH*} \rightleftarrows \text{RCN*} + \text{H}_2\text{O} \tag{5}$$

$$\text{RCN*} \rightleftarrows \text{RCN} + \text{s} \tag{6}$$

$$\text{H}_2\text{O}_2\text{*} \rightleftarrows \text{H}_2\text{O}_2 + \text{s} \tag{7}$$

$$2\text{H}_2\text{O}_2 \rightleftarrows 2\text{H}_2\text{O} + \text{O}_2 \tag{8}$$

where, R=  or , s=active site, and * means the adsorbed molecule.

It was assumed that aldehyde reacts with oxygen which is adsorbed in the molecular state on the active site of the catalyst.

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[5] J.R. Kittrell, R. Mezaki, and C.C. Watson, *Ind. Eng. Chem.*, **57**, 18 (1965).
[6] All calculations were carried out in Data Processing Center, Kyoto University.

Now if the adsorption processes as indicated by the Equations (1) and (2) are in equilibrium, and the rate controlling step is the surface reaction as represented by Equation (3), then the reaction rate for the nitrile formation is given by Equation (9):

$$\frac{dy}{d(W/F)}=\frac{kK_{\mathrm{R}}(1-y)K_{\mathrm{B}}(p_{\mathrm{Bo}}-1/2p_{\mathrm{Ro}}y)}{\{1+K_{\mathrm{R}}p_{\mathrm{Ro}}(1-y)+K_{\mathrm{B}}(p_{\mathrm{Bo}}-1/2p_{\mathrm{Ro}}y)\}^2}$$

where, p_{Bo} or p_{Ro}=partial pressure of oxygen and aldehyde at the top of catalyst bed, [atm]; y=yield of nitrile; k=rate constant of surface reaction, [atm·cm^3·g-cat^{-1}·min^{-1}]; K_R, K_B =adsorption equilibrium constant of oxygen and aldehyde, [atm^{-1}].

The values of k, K_{B} and K_{R} were estimated by the non-linear least square method. These values are shown in Table II, and the calculated curves (shown in Fig. 3 and 4) agree well with the experimental data. The value of rate constant of 2-thiophenealdehyde ammoxidation is almost twice to that of furfural ammoxidation. If the difference of temperature is taken into account, it can be concluded that the difference of the oxygen adsorption equilibrium constants is negligible in both cases.

TABLE II. Values of Constants

Reactant	k (atm·cm^3·g-cat^{-1}·min^{-1})	K_{R} (atm^{-1})	K_{B} (atm^{-1})
Furfural	25.92	20.67	3.022
2-Thiophenealdehyde	47.16	19.32	3.671

The increase in partial pressure of water, as shown in Fig. 5, decreased the yield of nitrile and hence effected the rate. However, in the rate expression, the effect of partial pressure of water has not been taken into account.

The mechanism from Equations (4) to (8) is assumed with the formation of oxime although this can not be accounted by this kinetic analysis.

Conclusion

The Mo-Bi-Sb (molar ratio 3: 5: 2) mixed oxide catalyst is most suitable for the vapor-phase ammoxidation of aldehyde group of furan and thiophene ring (*i.e.* furfural or 2-thiophenealdehyde), and the nitriles are produced selectively. The deactivation of this catalyst is negligible at high reactant conversion.

From the kinetic analysis, it is concluded that the ammoxidation of these aldehyde is controlled by the surface reaction between adsorbed aldehyde (furfural or 2-thiophenealdehyde) molecules and adsorbed oxygen molecules. The reaction rate constant of furfural ammoxidation is found to be one half to that of 2-thiophenealdehyde ammoxidation, whereas the equilibrium constants in both cases are found to be almost the same.

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